SEA WATER CONVERSION LABORATORY

UNIVERSITY OF CALIFORNIA

BERKELEY, CALIFORNIA

"Study of Permeability Characteristics of Membranes"

Quarterly Report No. 14

July 15, 1971

K. S. Spiegler, Principal Investigator
R. M. Messalem
R. J. Moore
J. Leibovitz (part-time)

Contract No. 952109
Jet Propulsion Laboratory
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ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

Pressure-permeation experiments were performed with the concentration-clamp cell. Streaming potentials and hydraulic permeabilities were measured for an AMF C-103 cation-exchange membrane bounded by 0.1 N NaCl solutions.

The streaming potential calculated from the slope of the recorded potential differences versus the applied pressure, yields a value of 1.895 millivolt/dekabar. No earlier data for streaming potentials across AMF C-103 membranes could be found in the literature. When comparison with other membranes of similar characteristics could be made, good agreement was found. A streaming potential value of -1.69×10^{-3} volt dekabar^{-1} was compared with the electroosmotic permeability at zero pressure of 2.3×10^{-3} cm^3 amp^{-1} sec^{-1}, which was previously measured with the same membrane. By Saxen's law (which is, in effect, one of Onsager's reciprocity relations), these quite different experiments should yield identical values when expressed in equivalent units, in this case, volt dekabar^{-1} and cm^3 amp^{-1} sec^{-1}. The discrepancy is not large in view of some possible changes of the membrane polymer structure brought about by application of different forces in the two types of measurement.

The values of the hydraulic permeability varied somewhat with the applied pressure difference and are between 1.3×10^{-8} and 3.9×10^{-8} cm^2/dekabar-sec. The specific hydraulic permeabilities, $\mathcal{P}$, were also

calculated and compared with data from the literature. Here again, no data were found for the AMF C-103 membrane but when data for different membranes with similar characteristics were checked, fair agreement was found.

The diffusion coefficient of the chloride ion in the AMF C-103 membrane was calculated, using Fick's first law of diffusion based on ion concentrations calculated from the Donnan equilibrium concentration of Cl^-. Dialysis data, measured previously were used and yield 1.69×10^{-7} cm^2/sec for a concentration difference of 0.1 - 0.05 N NaCl, and 1.23×10^{-7} cm^2/sec for 0.5 - 0.1 N NaCl. These values were compared with chloride ion self-diffusion coefficients measured by others in a similar cation-exchange membrane, which yielded similar values.

The following recommendations are made:

(a) More data on the dependence of the hydraulic permeabilities and streaming potentials on pressure are required.

(b) Pressure-permeation experiments with a concentration gradient across the membrane should be performed, in order to check whether additivity of fluxes could be obtained when different forces (including pressure gradients) are applied.

List of Symbols

A	Area of spherical segment, cm^2
a	Radius of circular base of spherical segment, cm
C	Concentration, mole cm^{-3}
D	Diffusion coefficient, cm^2 sec^{-1}
d	Adjusted membrane thickness, cm
d_o	Membrane thickness at $\Delta P = 0$, cm
ΔE	Total electromotive force between Ag/AgCl electrodes, volt
f	Molar activity coefficient
h	Altitude of spherical segment, cm
i	Current density, amp cm^{-2}
J	Flux of species designated by subscript, mole cm^{-2} sec^{-1}
J_V	Volume flux, cm sec^{-1}
L_p	Hydraulic permeability, cm $dekabar^{-1}$ sec^{-1}
P	Pressure, dekabar (= 9.869 atm)
$\mathcal{P}$	Specific hydraulic permeability, cm^2 $dekabar^{-1}$ sec^{-1}
r	Radius of sphere, cm
V	Volume of spherical segment, cm^3
X	Concentration of fixed charges in membrane, eq cm^{-3}
Z	Distance across membrane, cm
β	Electroosmotic permeability, cm^3 amp^{-1} sec^{-1}
Δ	Denotes difference, right minus left
μ^c	Chemical potential due to concentration only

Superscripts

'	Single prime denotes "property of the salt-receptor half-cell" (left side)
"	Double prime denotes "property of the salt-donor half-cell" (right side)
-	(overbar) denotes "in the membrane"

Subscripts

+	Cation
-	Anion
ext	External

I. Introduction

This is the fourteenth quarterly report of a research program designed to (a) construct one apparatus in which transport of salt, ions and water across membranes can be determined with differences in concentration, electric potential and pressure as driving forces, together with the measurement of membrane and streaming potentials, and (b) perform a variety of transport measurements in it to determine the range in which linear relationships between fluxes and forces exist. This permits us to study the performance of separators and membranes from a minimum number of basic characterization measurements. The experimental system has been described in the first annual report (November, 1968) and in the extended eighth quarterly report (January, 1970) which serves as the second annual report. Minor alterations in this system have been reported in the extended twelfth quarterly and annual report (January, 1971), together with the description of a cell measuring the a.c. (alternating-current) electrical conductivity of the membrane.

This report describes the progress made in the pressure-permeation experiments. Streaming potentials and hydraulic permeabilities were measured under experimental conditions, $\Delta\mu^c = 0$, $\Delta E_{ext} = 0$, that is, with pressure difference, ΔP, the only applied force. The measured streaming potential (at negligible current withdrawal) is compared with the electroosmotic permeability at zero pressure difference (as calculated from previous electromigration - electroosmosis experiments). Saxen's relation

is a statement of the equality of streaming potential and electroosmotic transfer:[1]

$$-\left(\frac{\Delta E}{\Delta P}\right)_{i=0} = \left(\frac{J_V}{i}\right)_{\Delta P=0}$$

The diffusion coefficient of the chloride ion in the AMF C-103 membrane was calculated using Fick's first law of diffusion as applied to chloride concentrations in the membrane calculated from the Donnan equilibrium equation.

II. Pressure-Permeation Experiments

Most of the work during the period covered by this report was devoted to experiments on ion and water transport under pressure. The pressure-permeation measurements were performed at uniform concentration ($\Delta\mu^C = 0$, C' = C" = 0.1 N NaCl) as the first step in a series of experiments. Because volume flow in these experiments was low, the percentage error due to measuring techniques was larger than in a higher-flow electroosmosis experiment. In the current experiments we used an accurate volumetric rather than gravimetric method to measure flow rate. The cell is fitted with a graduated 1 ml pipette bent so that the body of the pipette is horizontal, about 4 cm above each cell half. Since the pipettes are horizontal,there is no change in hydrostatic pressure with change in volume; since the bore of the pipette is only about 3 mm in diameter,there is less loss due to evaporation

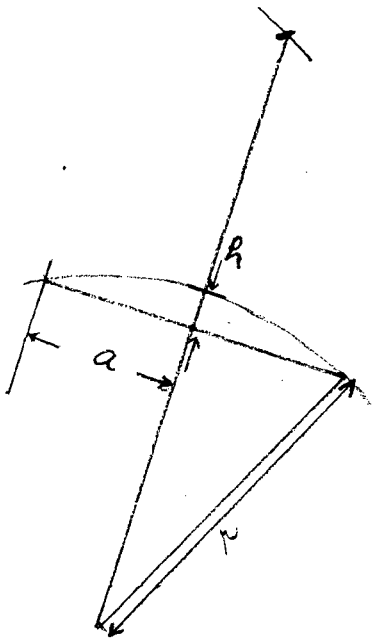
than when using the weighing bottle, whose diameter is 2.5 cm. When performing experiments expected to yield flows greater than 1 milliliter, however, we shall continue to use the gravimetric measurement.

Some difficulties arose due to two limitations of our apparatus: (a) the AMF C-103 cation-exchange membrane used has a high flow resistance due to its dense structure, and, (b) there is a pressure limitation imposed by the plastic structural material of the cell. It appears that non-linear, non-reproducible expansion phenomena occur in "Lexan" (General Electric Co., Pittsfield, Mass.) when these parts are subject to pressure differences above 1.5 atm. On the other hand, the cell could not be built from steel or another strong metal, since this would not have been suitable for the other transport measurements; all these were to be carried out under conditions of identical cell geometry.

II.1. Hydraulic Permeability

Measurements of hydraulic permeability were performed. Accuracy was substantially improved by the development of a method to determine corrections due to the membrane bulging through the small support holes. Both the measured flow and the correction are of the same order (0.01 $cm^3\ hr^{-1}$). Hence the bulging correction has to be very carefully measured. Reduction of this effect by using a membrane support with holes of smaller diameter is not considered desirable because of the increased danger of insufficient turbulence in the diffusion layer at the membrane-solution interface.

The bulging of the membrane and the deformation of the membrane support under application of a pressure difference were estimated from values of volume displacement as given below. Postulating that the volume displaced by the deformed membrane through the support hole approximates a segment of a sphere, and given the pore radius, it is possible to calculate the new surface area of the membrane, using the following from the Handbook of Physics and Chemistry:[2]



$$(1/6)\pi h\ (h^2 + 3a^2) = V = 1/3\ \pi h^2\ (3r - h) \quad (1)$$

$$2\ \pi\ r\ h = A \quad (2)$$

$$a^2 + (r - h)^2 = r^2 \quad (3)$$

where

V = volume of segment

A = surface area of segment

r = radius of sphere

a = radius of circular base of segment = 0.14108 cm

h = altitude of segment

Rearranging eq. (1) we obtain:

$$h^3 + 3ha^2 = 6V/\pi \tag{4}$$

Since it is reasonable to assume that in our membrane $h \ll a$, and since h is small, we neglect the h^3 term; equation (4) then becomes,

$$h = 2V/(\pi a^2) \tag{5}$$

Combining eq. (3) with eq. (2) gives

$$A = \pi (a^2 + h^2) \tag{6}$$

and eq. (5) and eq. (6) yield

$$A = \pi a^2 + [4V^2/(a^4\pi)] \tag{7}$$

From the measured volume increase, V, we can calculate h [eq. (5)] and then A [eq. (6)]; the results of these calculations are listed in Table 1.

The volume displacement is observed as the decrease in volume of the buret compartment which occurs after the pressure difference is removed. It is assumed that at the relatively low pressure involved here any measured volume decrease is due to the change in shape of the membrane rather than of the half-cell.

TABLE 1

MEMBRANE DEFORMATION DUE TO PRESSURE

Pressure Difference (atm.)	Total Volume Displaced (Measured) ($cm^3 \times 10^3$)	Volume Displaced per Membrane Segment (130 segments) ($cm^3 \times 10^3$)	Height of Spherical Segment from eq.(5) (cm)	Surface Area of Spherical Segment (cm^2)	Total Membrane Area (cm^2)
0.0	0	0.00	0.000	0.06253	8.129
0.2	80 ± 10	0.60	0.0192	0.06368	8.279
0.4	140 ± 5	1.08	0.0345	0.06628	8.616
0.6	230 ± 10	1.77	0.0566	0.07260	9.438
0.8	300 ± 25	2.31	0.0789	0.07968	10.360
1.0*	365 ± 5				
1.2*	480 ± 50				

* These were observations made in a single experiment only; other observations repeated 1 - 3 times.

If the bulging of the membrane through the small support holes were hemispherical, the volume displacement would be 532 μl. Table 1 shows that the volume displacement at the higher pressure differences approaches this value.

The specific hydraulic permeability, $\mathcal{P}$, is defined as the flow of solvent (in cm^3/sec) passing through a hypothetical membrane cube of edge length one centimeter under a pressure difference of one dekabar. This is a material property. We have presented evidence that with our experimental conditions the membrane has an increased surface area when subjected to pressure forces across it. If mass is conserved, and given constant density, a given increase in surface area should be accompanied by an equivalent decrease in membrane thickness. Referring to equation (7), the fractional increase in area may be expressed as

$$(4V^2/a^4\pi)(\pi a^2)^{-1} = 4V^2/(a^6\pi^2) \qquad (8)$$

The adjusted membrane thickness, d, would be

$$d = d_o\,(1 - 4V^2/a^6\pi^2) \qquad (9)$$

with the thickness at zero pressure difference, d_o, equal to 0.0175 cm, an experimental value.

This formula yields the values for the membrane thickness listed in Table 2.

TABLE 2

MEMBRANE THICKNESS AS A FUNCTION OF PRESSURE DIFFERENCE

Pressure Difference (atm)	$\frac{4V^2}{a^6\pi^2}$ (dimensionless)	d (cm)
0.2	0.016	0.0173
0.4	0.064	0.0164
0.6	0.160	0.0148
0.8	0.320	0.0125

In Table 3, the hydraulic permeability, L_p, and the specific hydraulic permeability, $\mathcal{P}$, as calculated from our experiments, are compared with those found by Lakshminarayanaiah[3] and by Scattergood and Lightfoot[4], both of whom studied AMF C-103 membranes at pressure differences between two and four atmospheres.

TABLE 3

COMPARISON OF HYDRAULIC PERMEABILITY VALUES

AMF C-103 Membrane (25°C)

	$L_p \times 10^6$ $\frac{\text{cm}}{\text{dekabar-sec}}$	d cm	$\mathcal{P} \times 10^8$ $\frac{\text{cm}^2}{\text{dekabar-sec}}$
Scattergood and Lightfoot[4]	1.073	0.0196	2.10
Lakshminarayanaiah[3] (supported membrane)	3.3	0.0152	5.02
Lakshminarayanaiah[3] (unsupported membrane)	5.9	0.0152	8.97
This study	2.89	0.0164	4.74
	3.92	0.0148	5.80

II.2. Streaming Potential

The streaming potential was measured across the AMF C-103 membrane bounded with 0.1 N NaCl solutions. As expected from previous experiments of the principle investigator,[5] problems of stability and reproducibility of small potential differences (of the order of 0.5 mv/atm) arose at the relatively low pressures employed. These problems were overcome by eliminating current leakage through ground loops.

Streaming potentials were measured using the large Ag/AgCl working electrodes instead of the less stable small electrodes originally prepared. When pressure differences up to 1.4 atm in 0.2 atm increments were applied, stable and reproducible electric potential differences were recorded.

The voltage measured prior to the application of pressure, i.e., the asymmetry potential, was subtracted from the observed potential difference. The pressure effects on the Ag/AgCl electrodes were neglected. The measured potential differences were plotted versus the applied pressure. A linear relationship was obtained, and the slope, after suitable conversion of units, yielded the following value for the streaming potential:

$$(\Delta E/\Delta P)_{i=0} = -173.13 \times 10^{-6} \text{ volt/atm} = -1.69 \times 10^{-3} \text{ volt/dekabar}$$

The present technique represents a significant advance over that used one year ago when a non-monotonous, non-linear relation of streaming potential versus pressure was observed.

The streaming potential was compared to the electroosmotic transfer, β, which we measured previously with the same membrane. By Saxen's law (which is, in effect, one of the reciprocity relations) these quite different experiments should yield the same results when converted to identical units. The electroosmotic permeability evaluated from an electromigration $\leftrightarrow$ electroosmosis experiment where the equilibrating salt solution is 0.1 N NaCl and an electric current density of -1.0 ma/cm^2 is applied was: $\beta = 2.3 \times 10^{-3}$ cm^3/amp-sec (Quarterly Report No. 13, Table 1). While this difference is not large, it does indicate some dependence of the transport coefficients on the type of force applied to the membrane. It should be kept in mind that the membrane is a non-rigid polymer structure.

III. The Diffusion Coefficient of Sodium Chloride in the Membrane

By postulating the presence of a Donnan equilibrium at the membrane-solution interface, and simplifying the equilibrium equation by neglecting the deviations from unity of the molar activity coefficients, $f_{\pm}$ (in the bulk), and $\bar{f}_{\pm}$ (in the membrane), it is possible to obtain approximate values for the chloride ion concentrations in the membrane.[6],[7]

If C_+ = sodium ion concentration

C_- = chloride ion concentration

X = concentration of fixed charges in the membrane

$\bar{\ }$ = (overbar); used to designate concentration of mobile ion in the membrane

then

$$\bar{C}_- = 2C_- \Big/ \left[X/C_+ \pm \sqrt{(X/C_+)^2 + 4} \right] \qquad (10)$$

Equation (10) is an expression for the chloride ion concentration in the membrane, $\bar{C}_-$, in terms of the concentration of fixed charges in the membrane, X, and the sodium and chloride ion concentrations in the bulk, C_- and C_+ respectively.

The concentration of fixed charges in the membrane may be computed from data presented in the fifth quarterly report:

$$X = (\text{capacity})\ (\text{density of wet membrane})\ (\text{thickness})^{-1}$$

$$X = (1.18 \times 10^{-3}\ \text{eq/gm})\ (0.01815\ \text{gm/cm}^2) \Big/ (0.0178\ \text{cm})^{-1}$$

$$= 1.20 \times 10^{-3}\ \text{eq/cm}^3$$

Using this value of X, one may compute the following values for chloride ion concentration in the membrane:

TABLE 4

CHLORIDE ION CONCENTRATION IN THE MEMBRANE

$[NaCl]_{bulk} = C_+ = C_-$ mole/cm^3	Chloride concentration in Membrane, $\bar{C}_-$ mole/cm^3
0.05×10^{-3}	2.08×10^{-6}
0.10×10^{-3}	8.28×10^{-6}
0.50×10^{-3}	1.81×10^{-4}

Using experimental values for salt flux during dialysis, the calculated concentrations for ions in the membrane, as listed in Table 4 above, and writing Fick's first law of diffusion as,

$$J = -\bar{D}_{-}(\Delta\bar{C}/\Delta Z)$$

one may calculate the diffusion coefficient for chloride ion in the membrane, $\bar{D}_{-}$. This has been done for two different dialysis experiments. The results are tabulated below and are compared with the chloride ion self-diffusion coefficients found by Caramazza et al[8] who used radioisotopes to study diffusion across a similar cation exchange membrane.* The membrane used by Caramazza et al consisted of the sodium form of sulphonated polystyrene, swollen with polyethylene and cross-linked with divinylbenzene. The exchange capacity of their membrane was 0.8 meq/gm, whereas the exchange capacity for the homogeneous polyethylene base AMF C-103 membrane used for our study was 1.18 meq/gm.

*The justification for the comparison of the self-diffusion coefficient of NaCl with the diffusion coefficient of NaCl in the membrane is as follows: because of the large excess of Na^+ over Cl^- in the membrane, diffusion of NaCl is primarily determined by the minority ion, Cl^-. It should be noted that in spite of this consideration, exact agreement should not be expected, since the two diffusion processes are different, and so are the membranes. It is therefore of interest that the two diffusion coefficients are so similar.

TABLE 5

COMPARISON OF CHLORIDE DIFFUSION COEFFICIENT AS FOUND BY TWO METHODS ($25^{o}C$)

DIALYSIS (this report)		SELF-DIFFUSION (Caramazza et al)	
Concentrations of solutions bracketing membrane	$\bar{D}_-$	Concentration of equilibrating solutions	$\bar{D}_-$
(mole/cm^3 x 10^3)	(cm^2/sec)	(mole/cm^3 x 10^3)	(cm^2/sec)
0.05 ↔ 0.10	1.69×10^{-7}	0.2	1.95×10^{-7}
0.10 ↔ 0.50	1.23×10^{-7}	0.6	2.82×10^{-7}

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